

CALCIFICATION PREVENTION TABLETS

Geoffrey A. Lindsay and Michael A. Hasting
Chemistry Division, Research Department
Naval Weapons Center, China Lake, CA 93555

and
Michael A. Gustavson
NAVSEADET (PERA CV)
Bremerton, WA 98310-4924

ABSTRACT

Citric acid tablets, which slowly release citric acid when flushed with water, are under development by the Navy for calcification prevention. The citric acid dissolves calcium carbonate deposits and chelates the calcium. For use in urinals, a dispenser is not required because the tablets are non-toxic and safe to handle. The tablets are placed in the bottom of the urinal, and are consumed in several hundred flushes (the release rate can be tailored by adjusting the formulation). All of the ingredients are environmentally biodegradable. Mass production of the tablets on commercial tableting machines has been demonstrated. The tablets are inexpensive (about 75 cents apiece). Incidences of clogged pipes and urinals were greatly decreased in long term shipboard tests. The corrosion rate of sewage collection pipe (90/10 Cu/Ni) in citric acid solution in the laboratory is several mils per year at conditions typically found in traps under the urinals. The only shipboard corrosion seen to date is of the yellow brass urinal tail pieces. While this is acceptable, the search for a nontoxic corrosion inhibitor is underway. The shelf life of the tablets is at least one year if stored at 50% relative humidity, and longer if stored in sealed plastic buckets.

INTRODUCTION

This project grew from the problem of calcium carbonate buildup in the collection, holding and transfer (CHT) piping (i.e., the ship's sewer system) and plugged urinals on the U.S. Navy's aircraft carriers. Sea water is used to flush toilets on ships. When sea water mixes with urine, it precipitates calcium salts which are insoluble and form hard deposits when the pH of the water is above about 6 (sea water has a pH of about 8.5 depending on the dissolved gases). Acids have been shown to dissolve the calcium deposits in the sewage piping. The treatment used on aircraft carriers has been to place in the urinals a perforated plastic bag of sulfamic acid powder held in a plastic dispenser. It is only marginally effective in removing calcification in the pipes. For aircraft carriers, nearly one million dollars annually is consumed with hydroblasting of clogged pipes. There are other costs associated with fleet down-time which are not easily quantified. Sulfamic acid powder is a very strong acid; hence, it presents an irritation and potential safety hazard to the user. It is difficult to determine when the bags of sulfamic acid are depleted, and the sailors dislike removing the used bags from the plastic dispensers in the urinals.

This paper describes the three-year development and testing of citric acid tablets, tablet manufacturing trials and shipboard decalcification trials. The shipboard tests had an immediate impact on the sailors by reducing the incidence of plugged urinals.

TABLET DEVELOPMENT

Design Criteria. We set the following requirements for developing calcification prevention tablets. The ingredients should be: (1) water soluble, (2) biodegradable, (3) nontoxic, and (4) commercially available. The tablets should: (5) be manufacturable on commercially available equipment by more than one company, (6) give a slow, controlled rate of acid release, (7) be mechanically strong, (8) be low cost, and (9) not require a dispenser.

Attempts to bind sulfamic acid into a tablet were abandoned in favor of citric acid for a number of reasons: (1) citric acid is more environmentally acceptable, (2) citric acid is a chelating agent for calcium, (3) citric acid tablets have superior mechanical integrity, and (4) the total cost is essentially equivalent.

Comparison of Water-Soluble Binders. A large number of synthetic and natural water-soluble polymer binders, including poly(vinyl alcohol), carboxymethyl cellulose, xanthan gums, were investigated in the laboratory and found to be unsuitable due to poor binding or poor release qualities. We found that polyethylene oxide (PEO) gave the best balance of dissolution rate control, manufacturability, availability, and environmental acceptance.

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Other Additives. The kinds of additives which we believe are important are: 1) high molecular weight (PEO) binders (for release rate control), 2) compatible processing aids (calcium stearate), 3) hardness control additives (sorbitol and PEG), 4) desiccants (fumed silica), and 5) corrosion inhibitors. We are currently screening corrosion inhibitors for 90/10 Cu/Ni pipe. We recommend excluding coloring agents, perfumes and deodorants. Coloring could splash and stain white Navy uniforms. Odors, which could indicate deteriorating vent piping which must be repaired to prevent dangerous accumulations of hydrogen sulfide gas, should not be masked.

Selecting the Formulation. The present preferred tablet formulation, which provides a pH of about 4.0 to 4.5 in the shipboard urinals, is: citric acid = 70%; PEG = 16%; Sorbitol = 10%; PEO = 3.5%; Ca stearate \leq 0.25%, and fumed silica \leq 0.25%

Biodegradability of Tablet Ingredients. Citric acid, calcium stearate,¹ and sorbitol² are readily biodegradable (>60% in 10 days). The solubility of calcium stearate is 2 mg/l which is sufficient to ensure availability to bacteria. Polyethylene glycol (PEG) biodegrades slowly.³ Polyethylene oxide (Polyox^R), a higher molecular weight form of PEG, will also biodegrade with time. Silica in many forms, including quartz, can be metabolized by biological action.⁴ For example, several bacteria and plants can produce monomer silica from quartz and other solid (polymer) forms of silica. The resulting monomer silica is taken up by various life forms (eg., diatoms) and used for skeletal material. The lethal oral dose of sulfamic acid for rats is 1.6 g/kg.⁵

Solubility. The saturation solubility of citric acid in water at 10 °C (50 °F) is about 54 grams per 100 grams of solution, and at 80 °C (176 °F), about 79 grams per 100 grams of solution. Hence, dissolved citric acid is available in high concentrations. The chelation property of citric acid causes it to bind tightly to calcium ions. The solubility of calcium citrate in sea water is low; however, the insoluble calcium citrate is a soft, hygroscopic solid which is easily suspended and flushed out of the system.

pH Control. The pH determines the kinetics of calcium dissolution and pipe corrosion more than any other variables, such as temperature and buffering ingredients. We have found that citric acid has a dampening effect on the pH swings. Whereas, in dissolution tests with sulfamic acid, the pH jumps up and down to a much greater extent. The same spiked pH phenomenon was observed in shipboard field tests with sulfamic acid.

TABLET PERFORMANCE TESTING IN THE LABORATORY

Controlled Release Rate of Acids. A laboratory test for measuring the dosage of acid released from the tablets under controlled conditions which simulate actual shipboard urinal conditions was developed. The laboratory dissolution rate tester, shown in figure 1 on the next page, evolved from several earlier prototypes. The release rate of citric acid was determined by recording the pH in the 0.7-liter overflow vessel until the tablet was essentially dissolved. Tap water or sea water⁶ (0.5 liters/flush) was used. The flow rate was adjusted to give about one flush every 60 seconds. The temperature of the water was between 75 and 85° F. The tablets should maintain sea water between a pH of about 3.2 ± 0.2 to about 5.4 ± 0.2 (in the 0.7-liter overflow container) for about 250 ± 50 flushes to meet our specifications.

Citric acid tablets were made with various amounts (and various molecular weights) of PEO, PEG and citric acid to find compositions which gave desirable release rates and mechanical integrity. At constant PEO to citric acid ratio, the release rate was essentially unchanged by sorbitol, the hardening agent. After considerable testing, we felt that 3.5% PEO would be the most effective composition in controlling the calcification of the shipboard CHT lines. From all the data collected, both in the lab and on the ship, a tablet formulation was selected for scale-up. The main purpose of the scale-up runs were to determine if citric acid tablets could be mass produced. Several manufacturers have now successfully produced several hundred thousand tablets which are three inches in diameter and about one-inch thick (145 grams of ingredients). This tablet size is about as large as can be conveniently manufactured on commercial equipment, and the tablet gives two to three days of service in heavily used urinals.

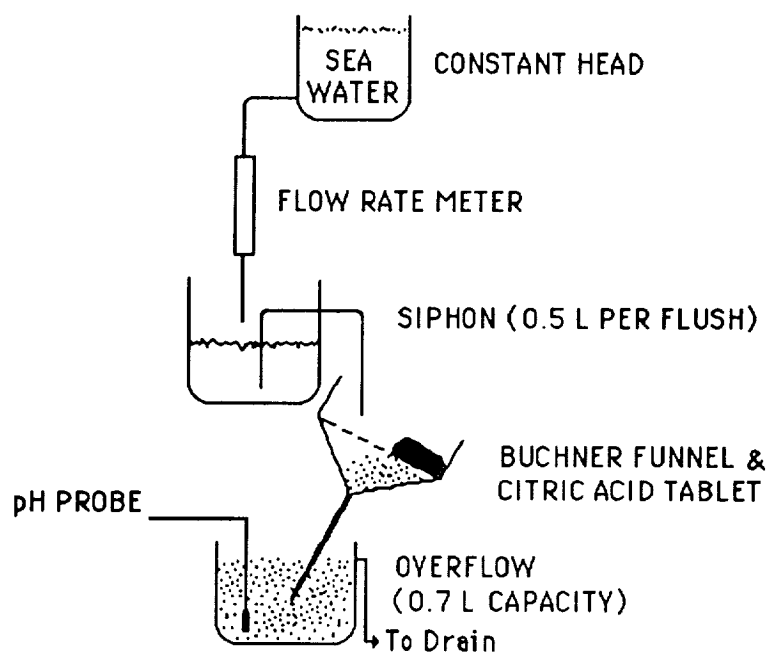


Figure 1: Laboratory Dissolution rate tester

TABLETING PROCESS DEVELOPMENT

Comparison of Various Processes. The process of making the tablets went through several stages. At first citric acid was mixed with the binders at room temperature, heated in a mold above the melting point of the binders, placed in a hydraulic press and cooled under pressure. This worked well, but we found that making tablets by room temperature compression was a more efficient process. It was discovered that combining a mixture of the ingredients as powders into a die and subjecting it to several tons of pressure, the tablets would retain shape in water and slowly dissolve at desirable rates.

Effect of Temperature and Humidity in the Manufacturing Process. It was found that high humidity greatly reduces the ability to manufacture high quality tablets. Relative humidity in the tableting room should be keep below 25%. If the relative humidity is too high, citric acid, which is anhydrous, will attract moisture from the atmosphere. In the press, the moisture is squeezed out of the citric acid which makes the binder tacky. Although dry-to-the-touch, under the pressure of the tableting process, the tablets may stick to the die.

The addition of a small amount of a desiccant to the tablet aids the binder tableting process, eg., about 1/4% or less of fumed silica. In addition to this, about 1/4% or less of calcium stearate is added to act as a die-lubricant and to help with the sticking problem. After the tablet is sealed in its plastic wrapper it takes several months of exposure to humidities above 75% before the tablet is effected by the moisture. After prolonged exposure to high humidity, the tablet softens, but its performance in the urinal is unaffected. The plastic-wrapped tablets are stored in a polyethylene bucket which is sealed from the environment. Even though the tablets are manufactured and packaged in a very low humidity environment, we believe a desiccant pack should be added to the container in order to absorb any moisture that may get into the container if the lid is not properly resealed.

CITRIC ACID TABLET PERFORMANCE

Reactions with calcium carbonate. After two months of treatment with citric acid tablets in shipboard tests, it was found that hard build up in the pipes was greatly softened, and the soft build up was very easy to remove by flushing. Although it has not yet been analyzed, the soft build up is likely to be calcium citrate based on the following. Citric acid reacts with calcium carbonate giving off carbon dioxide and various forms of calcium citrate. The solubility of tricalcium citrate tetrahydrate ($\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2$ plus 4 moles of water of crystallization) is reported

to be 0.85 grams per 100 cc water at 18° C and less at higher temperatures.^{7,8} In the presence of excess citric acid, the tricalcium salt is in equilibrium with the dicalcium hydrogen salt which is thermodynamically preferred⁹ in warmer water: $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 + \text{citric acid} \rightleftharpoons \text{CaH}(\text{C}_6\text{H}_5\text{O}_7)$.¹⁰ The dicalcium hydrogen salt may be more soluble, but no data on its solubility has been found. The pH and other buffering agents will also play an important role in the kinetics of calcium carbonate dissolution and calcium citrate precipitation. To learn more about solubilities, the following tests were run.

We obtained samples of calcified solids which had formed in the CHT pipes of aircraft carriers when the ship had been using only sulfamic acid bag treatment. (The citric acid tablets had not been invented when these samples were obtained.) The solids are mostly calcium carbonate, but are also thought to contain calcium oxalate, uric acid, and other calcium salts.¹¹ About one gram of the calcified solid was placed in 100 ml of a seawater-solution containing various amounts of the acid to be tested. The time to completely dissolve the calcified solid was measured. The tests in our laboratory at room temperature, showed that one or more part of citric acid per part of solid dissolved the solid in a few minutes giving off bubbles (CO_2) and leaving behind a brown cloudy solution.

The results from controlled experiments using pure materials are shown in Table I. The amount of pure CaCO_3 was held constant at 1.38 grams (0.01235 moles) per 100 cc tap water at room temperature.

Test #	Acid type	Acid/Ca (mole ratio)	Comments
1	pure citric	0.74	solution did not become clear
7	pure citric	1.01	clear in 30 min.; ppt. in 60 min.
10	pure citric	1.30	clear in 7 min.; ppt. in 25 min.
9	pure citric	1.56	clear in 4 min.; ppt in 2 hours.
12	pure citric	2.08	clear in 3 min.; ppt in 2 days.

It would appear that citric acid is effective in dissolving hard calcium deposits, and forms some fine particles suspended in water at these concentrations (probably calcium citrate) which could be flushed through the pipes into the holding tank.

Mechanical Properties of Tablet. A quick and dirty test was devised which simulates conditions likely to be encountered in the field. Tablets are dropped on a hard floor (vinyl tile-covered concrete) from a three-foot elevation. If the tablet does not break, crack or chip or produce more than 2% loose powder, it passes.

A more scientific test will be initiated, if problems arise. One such test would be to support the tablet with two parallel bars and drop a heavy dart from known heights, increasing the height until the tablet breaks. The energy to break the tablet can be determined statistically (eg., the foot-pounds of force at which 50% of the tablets from one lot survive).

Long Term Aging. Several lots of citric acid tablets, in their Mylar^R wrapper, were stored at room temperature in a plastic bucket with its lid cracked open, thus exposing tablets to variable humidity conditions in a Los Angeles warehouse. After one year, they were tested for dissolution rate vs pH, and breakage resistance. The flushes per tablet for these 3% PEO formulations ranged from 180 to about 220 for the year-old tablets; whereas, the fresh tablets lasted about 240 to 280 flushes. However, it should be noted that the temperature of the flush water used for the aged tablets was 30° C compared to only 23° C for the fresh tablets. The temperature difference could account for most of the difference in number of flushes. The tablets passed the breakage test.

A dozen wrapped tablets (3% PEO), were stored in a chamber at a constant 50% relative humidity at room temperature for one year. After one year, the tablets were noticeably softer (fingernail indentation test). The dissolution rate ranged from 300 to 350 flushes over the required 3 to 5.5 pH range using 28° C tap water. These data would indicate that the tablets have a shelf-life of at least one year. We speculate that exposing the tablets to humid air over long periods may decrease the dissolution rate due to "solvent-welding" of the citric acid particles with the binder, so that fewer discrete particles slough off the tablet, giving more time for the molecular dissolution of citric acid from the surface of the tablet.

PACKAGING CONSIDERATIONS

Because the tablets are water soluble and most storage aboard ship is very humid, care must be taken in the packaging of the tablets. To keep the tablets dry, each tablet is sealed in a plastic wrapper then placed in a five gallon plastic bucket. These buckets must be water tight, and in each bucket a desiccant package is added. A polyethylene bucket with an O-ring seal was chosen. After the bucket is opened aboard ship, this package of desiccant will absorb some of the moisture in the air, but is only effective if the bucket is sealed again with its original lid in a timely manner.

Even though the plastic wrapping acts as a barrier to water and moist air, it is understood that a small amount of water will diffuse through any plastic film over long periods of time. However, the buckets are the first line of defense against moisture. The wrapping is also gives mechanical protection to the tablets during packing, shipping and unloading of the buckets. We have had success with polyester (Mylar^R), polyethylene and related copolymers.

SHIPBOARD TESTING

From February, 1989 until present, many tests have been run in USS Independence (CV 62). In the first test aboard USS Independence, a bank of four urinals was used to test the pH and dissolution rates of the tablets. The pH in the urinals was measured as a function of various formulations of the citric acid tablet. Readings ranged from as low as 3 to around a high of 6. One could see when the ships crew got up in the morning and when they went to bed at night by the change in pH in the CHT lines. In the lines down stream from the urinals, the pH would drop as a urinal was flushed. But with the addition of the toilets' flow of water (about 15 times more volume), the pH would again rise to over seven.

A six month supply of the 3%-PEO formulation was given to USS Independence in March, 1990. The ships trouble logs show the rate of call for clogged urinals went from about four per day to about one per day after this supply of tablets was used by the ship. This proved to be of great benefit to the ships maintenance personnel as those sailors normally assigned to fixing the drains could now be used in other places on the ship. With the use of the 3% PEO tablets, enough citric acid was added to soften the calcification in the main pipes.¹² Several valves were pulled after the return of USS Independence from the Persian Gulf, and little-to-no calcification was found in the CHT system. The pipes had been cleaned by hydroblasting at least two years earlier and should have had major problems with the CHT system from calcification. Tests in USS Independence showed a usage rate of about 0.027 tablets per day per sailor, this number fits well with the calculated amount of tablets before the test began.

More controlled tests have been done in USS Nimitz (CVN 68) where valves have been pulled before the use of the citric acid tablets and the calcification measured and photographed in October, 1990 and February, 1991. After only two months of citric acid tablet use, softening of the calcification and removal of some of the calcification had taken place.

Response from the aircraft carriers has been very favorable, with the only problems being corrosion of the tail pieces of the urinals. The yellow brass tail pieces can be periodically replaced or a fiberglass tail piece can be used. We are also investigating adding corrosion inhibitors to the tablet formulation.

CORROSION TESTING OF 90/10 COPPER/NICKEL PIPE

The Naval Civil Engineering Laboratory (NCEL) was tasked to compare corrosion rates of 90/10 copper-nickel metal exposed to: (1) sea water as a control, (2) sea water containing a citric acid tablet, and (3) sea water containing sulfamic acid bag contents (NSN 9G-6850-01-150-4921). This test consisted of a placing 90/10 Cu/Ni coupons in sea water at 35°C (95°F) containing a given amount of acid and monitoring weight loss of the metal coupon with time. For the most severe case (a concentration of 2.9 g/L of each acid formulation), after two weeks, the corrosion rate for the citric acid tablet (70% citric acid) was 60 mpy, and that for sulfamic acid bag (95% sulfamic acid) was 80 mpy. The pH during these tests increased with time from about 2 to about 5 for both acids. The report concludes that, at the most severe condition, corrosion due to citric acid tablets was about the same as that for sulfamic acid bag contents (NSN 9G-6850-01-150-4921). The results of this test were reported in reference.¹³

We ran another corrosion test in which the pH was held relatively constant for three weeks by adding more acid as it was consumed (as indicated by a rise in pH). The test protocols used are described in ASTM G 1-90 and ASTM G-31-72. A summary of the data are shown in the table below. The smaller corrosion rates in the NWC test compared to the NCEL test probably results from the lower temperature of the water (23° vs. 35° C).

Table II. Corrosion Rate of 90/10 Cu/Ni pipe in Various Acidic Solutions				
Fluid Id.	Solution Type	pH	Corrosion Rate: mil/yr.	Comments (final color of water)
R-010042	tap water	8	0.01	washed + scrubbed 7X
Q-283240	synth. sea water	8	0.47	light blue, ppt
C-143637	pure sulfamic acid	3	7.25	light green
E-434651	sulfamic acid baggie	3	6.20	green / yellow
A-161722	pure citric acid	3	29.5	dark green
I-213547	citric tablet	3	21.9	dark green
O-263139	citric tab + Na silicate	3	20.5	dark green
M-124550	citric tab + Na molybdate	3	20.3	dark green
K-495354	citric tab + benzotriazole	3	0.72	tan / green
D-070910	pure sulfamic acid	5	2.04	light green
F-030008	sulfamic acid baggie	5	1.85	yellow
B-131819	pure citric acid	5	1.54	green
J-253338	citric tablet	5	1.63	blue / green
P-042029	citric tab + Na silicate	5	1.33	blue / green
N-020523	citric tab + Na molybdate	5	2.36	blue / green
L-152430	citric tab + benzotriazole	5	0.03	tint of green

Three 1"x3" strips of 90/10 Cu/Ni pipe cut from a 5"-dia. schedule 40 pipe were submerged without stirring in Bio-Sea Marinemix⁵ (simulated sea water) at room temperature. The metal coupons were removed from the solution six or seven times for cleaning and weighing during the three-week test period. The corrosion rate at a pH of 3 is considerably higher than at a pH of 5 for all solutions. In order to hold the pH constant during the test, the solutions had to be mixed with concentrates of the acids periodically. This procedure resulted in the pH cycling to a somewhat higher value as the acid was consumed, then dropping to the desired value when the concentrate was added.

At the most severe conditions (pH = 3) citric acid corrodes at a higher rate than sulfamic acid, but at the milder conditions (pH = 5), the two acids are comparable. Measurements of pH on aircraft carriers in the sewage collection lines reveal pH ranges from 4 to 5 in the traps under the urinals and up to about 7 in the large mains. Yet the hard deposits in the mains had been reduced to soft, flushable deposits. Therefore, the citric acid treatment has been recommended for continued use.

Several corrosion inhibitors for citric acid tablets were tested. Note that benzotriazole (BTA) is an excellent corrosion inhibitor for citric acid even at the pH of 3 condition. Unfortunately, BTA is toxic: oral LD₅₀ for rats is 560 mg/Kg; dermal LD₅₀ for rabbits is 2g/Kg; and for sunfish, trout and minnows, the lethal dose is about 35 mg/l.¹⁴ Hence, we do not recommend putting BTA in the tablets. A National Cancer Institute report on feeding benzotriazole (BTA) to rats concluded that it was not carcinogenic in Fischer 344 rats, and there was inconclusive evidence in B6C3F1 mice.¹⁵ The sodium silicate and sodium molybdate appear to have no effect on corrosion rate by themselves.

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- ⁴ A.M. Lauwers and W. Heinen, *Arch. Microbiol.*, **95**, 67 (1974).
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- ⁶ For synthetic sea water, we used Bio-Sea Marinemix (available from California Aquarium Supply House, San Carlos, CA), a dry mixture of salts mixed with fresh water to a specific gravity of 1.020 to 1.023 at 73 to 77° F. It contained the following chemical abundances (in g/kg): chloride = 18.9; sodium = 10.5; sulfate = 2.47; magnesium = 1.27; calcium = 0.40; potassium = 0.38; bicarbonate = 0.14; bromide = 0.065; boric acid = 0.024; strontium = 0.008; silicic acid = 0.003; fluoride = 0.0013; and many other trace elements.
- ⁷ *The Merck Index*, P.G. Strecher, Ed., Merck & Co., Inc., Rahway, NJ, 1960; p.192.
- ⁸ *Handbook of Chemistry and Physics*; R.C. Weast and M.J. Astle, Eds.; CRC Press; Boca Raton, FL, 1980-1981; p. B-87.
- ⁹ Sometimes there is not enough time to reach the thermodynamically preferred compound, and kinetics dictates which form is found.
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